

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
4 January 2001 (04.01.2001)

PCT

(10) International Publication Number  
WO 01/01182 A1

(51) International Patent Classification<sup>7</sup>: G02B 13/14,  
9/00, F21V 9/06

[IN/US]; 59 E. Fourth Street, Corning, NY 14830 (US).  
PRICE, Michael [US/US]; 32 Park Lane, Big Flats, NY  
14814 (US). RIVERA, Michael [US/US]; 7302 Eden  
Brook Drive #215, Columbia, MD 21046 (US).

(21) International Application Number: PCT/US00/17165

(22) International Filing Date: 22 June 2000 (22.06.2000)

(74) Agent: MURPHY, Edward, F.; Corning Incorporated,  
Patent Dept. SP TI 3-1, Corning, NY 14831 (US).

(25) Filing Language: English

(81) Designated States (*national*): JP, KR, RU, US.

(26) Publication Language: English

(30) Priority Data:  
60/141,155 25 June 1999 (25.06.1999) US

(84) Designated States (*regional*): European patent (AT, BE,  
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE).

(71) Applicant (*for all designated States except US*): CORNING INCORPORATED [US/US]; 1 Riverfront Plaza,  
Corning, NY 14831 (US).

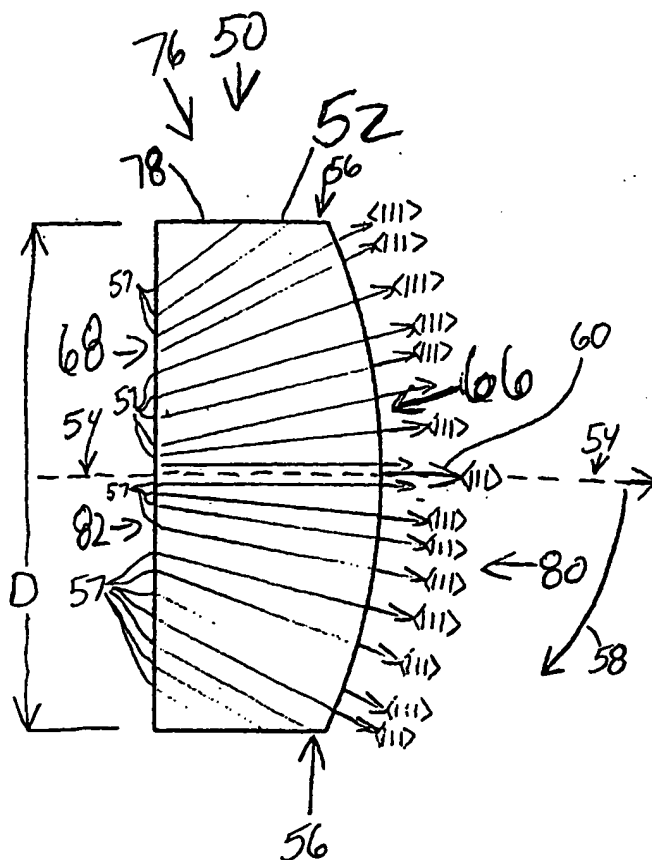
Published:  
— With international search report.

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): MEDA, Gautam

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: BIREFRINGENCE MINIMIZING FLUORIDE CRYSTAL OPTICAL VUV MICROLITHOGRAPHY LENS ELEMENTS AND OPTICAL BLANKS THEREFOR



(57) Abstract: A birefringence minimizing fluoride crystal VUV optical lithography lens element (50) is provided for use with lithography wavelengths less than 230 nm. The VUV lithography lens element has an optical axis encompassed by a lens perimeter with the fluoride crystal lens having a variation (58) in crystallographic orientation direction which tilts away from the optical center axis (54) towards the lens perimeter to provide minimal birefringence.

6,683,714

1/27,200

WO 01/01182 A1

BIREFRINGENCE MINIMIZING FLUORIDE CRYSTAL OPTICAL VUV  
MICROLITHOGRAPHY LENS ELEMENTS AND OPTICAL BLANKS  
THEREFORE

5                   CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of United States Provisional Application Serial No. 60/141,155, filed June 25, 1999, entitled Minimal Birefringence By Orientation Control, of Gautam Meda, Michael W. Price and Michael Rivera, the  
10 content of which is relied upon and incorporated herein by reference and the benefit of priority under 35 U.S.C. § 120 is hereby claimed.

BACKGROUND OF THE INVENTION

15   Field of the Invention

The present invention relates generally to optical lithography elements and blanks, and particularly to optical microlithography crystal lens elements and optical element blanks for use in optical photolithography systems utilizing vacuum ultraviolet light (VUV) wavelengths below 200 nm, preferably below 193 nm,  
20 preferably below 175nm, more preferably below 164 nm, such as VUV projection lithography systems utilizing wavelengths in the 157 nm region.

Projection optical photolithography systems that utilize the vacuum ultraviolet wavelengths of light below 200 nm provide benefits in terms of achieving

smaller feature dimensions. Such systems that utilize vacuum ultraviolet wavelengths in the 157 nm wavelength region have the potential of improving integrated circuits with smaller feature sizes. Current optical lithography systems used by the semiconductor industry in the manufacture of integrated circuits have progressed  
5 towards shorter wavelengths of light, such as the popular 248 nm wavelengths, but the commercial use and adoption of vacuum ultraviolet wavelengths below 200 nm, such as 193 and 157 nm has been hindered by the transmission nature of such vacuum ultraviolet wavelengths in these VUV excimer laser regions through optical materials. Available optical materials and their optical properties at such short lithography  
10 wavelengths have hindered the industrial utilization of the below 200nm wavelengths in optical lithography systems. The utilization of fluoride crystals such as calcium fluoride as optical lens blanks for and optical lens elements in optical lithography has been hindered by the birefringence of the fluoride crystal optical materials and the detrimental effect that the crystal's birefringence has on the lithography light  
15 transmitted through it. For the benefit of vacuum ultraviolet photolithography in the below 200nm wavelength 157 nm region such as the emission spectrum VUV window of a F<sub>2</sub> excimer laser to be utilized by the semiconductor industry in the manufacturing of integrated circuits there is a need for optical lithography fluoride crystal lens element members and optical member blanks with minimal birefringence.

20 European Patent Application EP 1001314A2 of the Nikon Corporation describes a durable optical system for projection exposure which utilizes calcium fluoride crystals for their superior durability against high irradiating lithography energy densities such as produced by a ArF excimer lithography laser. U.S. Patent 6,061,174 of the Nikon Corporation describes a lithography image focusing optical system for  
25 ultraviolet lasers with shorter than 300nm wavelengths which utilizes image focusing calcium fluoride crystal optical members with low sodium concentrations. Such systems have utilized calcium fluoride crystal lens elements with uniform <111> crystallographic orientation direction as shown in FIG. 4 herein. The prior art has not addressed the adaption of the fluoride crystal element to the lithography light beam it is  
30 manipulating.

The present invention overcomes problems in the prior art and provides beneficial lithography elements with beneficial optical properties and lithography

characteristics including minimal birefringence and blanks therefor that can be used to improve the lithographic manufacturing of integrated circuits with VUV wavelengths.

### SUMMARY

5

An embodiment of the invention comprises a birefringence minimizing fluoride crystal VUV optical lithography lens. The lens is preferably comprised of a single fluoride crystal. The fluoride crystal lens has an optical center axis encompassed by a fluoride crystal lens perimeter with the lens having a variation in crystallographic orientation direction which tilts away from an optical center axis  $\langle 111 \rangle$  direction orientation and towards the perimeter.

In further embodiment the invention includes a fluoride crystal optical lens. The fluoride crystal optical lens is comprised of a single fluoride crystal having a first optical lens surface and a second optical lens surface which opposes the first lens surface. The fluoride crystal has a progressive concentration of crystal dislocation defects that increases from the first optical lens surface to the second optical lens surface.

A further embodiment of the invention includes a calcium fluoride crystal optical element for manipulating a transmitting wavelength  $\lambda < 200$  nm. The calcium fluoride crystal optical element comprises a calcium fluoride crystal having a first optical surface and a second optical surface for manipulating the wavelength  $\lambda$  light. The calcium fluoride crystal has a concentration of crystal dislocation defects that increases from the second optical surface to the first optical surface. The first optical surface has a first surface subgrain boundary length per unit area in the range from about 10 to 50 cm/cm<sup>2</sup>. The second optical surface has a second surface subgrain boundary length per unit area  $< 10$  cm/cm<sup>2</sup>.

An embodiment of the invention includes a fluoride crystal lens blank comprising a fluoride crystal having a center axis through a large dimension D surface. The center axis and the large dimension D surface are encompassed by a blank perimeter. The center axis aligns and coincides with an optically preferred crystallographic direction of the fluoride crystal. The fluoride crystal lens blank has a

variation in crystallographic orientation direction which spreads out from the center axis and tilts away from the center axis and towards the blank perimeter.

A further embodiment of the invention includes a birefringence minimizing fluoride crystal optical lithography lens blank. The blank comprises a calcium fluoride crystal having a 193 nm internal transmission >99%/cm, a 157 nm internal transmission >99%/cm and a refractive index homogeneity no greater than 1 ppm. The calcium fluoride crystal has a plurality of non-parallel crystallographic <111> orientation and the blank has a center axis which coincides with a calcium fluoride crystal <111>. The blank has a crystal perimeter and a variation in crystallographic orientation direction wherein the angular deviation between the center axis and a given non-parallel crystallographic <111> orientation having a relative location between said center axis and the perimeter correlates to the relative location distance from the center axis. Preferably the angular deviation increases with an increase in distance from the center axis.

Another embodiment of the invention includes a fluoride crystal optical element blank. The optical element blank is comprised of a fluoride crystal having a diameter, a first diameter plane surface, a second diameter plane surface, and a crystal thickness defined by the first and second surfaces. The blank lens has a concentration of crystal dislocation defects that increases from the second surface to the first surface. The second surface has a second surface subgrain boundary length per unit area SS and the first surface has a first surface subgrain boundary length per unit area FS wherein  $FS > SS$ .

### BRIEF DESCRIPTION OF THE DRAWINGS

25

FIG. 1 shows embodiments of the invention in a lithography system/process.

FIG. 2-2H show embodiments of the invention in a lithography system/process with cross sectional views.

30

FIG. 3-3G show embodiments of the invention in a lithography system/process with cross sectional views.

FIG. 4 shows a cross sectional view of a calcium fluoride crystal lens element with an oriented uniform  $\langle 111 \rangle$  crystallographic orientation direction with light passing through the outer perimeter of the lens having a light path that is not parallel to the  $\langle 111 \rangle$ .

FIG. 5-5a shows cross sectional views of embodiments of the invention.

FIG. 6 shows the crystallographic orientations of a calcium fluoride crystal including the  $\langle 111 \rangle$  crystallographic orientation direction in accordance with the invention, with the small circles representing F and the large circles representing Ca.

FIG. 7-7a shows a cross sectional view of an embodiment of the invention including a progressive concentration of crystal dislocation defects and variation in  $\langle 111 \rangle$ .

FIG. 8 shows a cross sectional view of an embodiment of the invention including a progressive concentration of crystal dislocation defects.

FIG. 9-9a shows a cross sectional view of embodiments of the invention.

FIG. 10 shows an embodiment of the invention.

FIG. 11 is a photomicrograph of a calcium fluoride crystal surface.

FIG. 12 is a photomicrograph of a calcium fluoride crystal surface.

FIG. 13 shows an embodiment of the invention.

30

### DETAILED DESCRIPTION

The invention includes a birefringence minimizing fluoride crystal VUV lithography lens comprised of a fluoride crystal. As shown in FIG. 1, 2 and 3, fluoride crystal VUV lithography lens are utilized in VUV microlithography systems/processes 51 which preferably utilize VUV wavelengths of light  $<200$  nm. The fluoride crystal lens elements are utilized in the microlithography systems including the optics which make up the illumination system, preferably including the light source (which is preferably an excimer laser), and the projection system.

The fluoride crystal optical lithography lens 50 is comprised of a fluoride crystal 52, preferably a single crystal. As shown in FIG. 5, fluoride crystal optical lens 50 has an optical center axis 54 which is encompassed by a fluoride crystal lens perimeter 56. Fluoride lens 50 has a variation 58 in crystallographic orientation direction which tilts away from an optical center axis  $<111>$  direction orientation 60 towards perimeter 56. As shown in FIG. 5a and 7a the  $<111>$  crystallographic orientations 57 tilt away from optical center axis  $<111>$  direction orientation 60 and spread out towards perimeter 56.

In contrast to a variation in crystallographic orientation direction, lens 50' of FIG. 4 is comprised of a fluoride crystal 52' with an oriented uniformity in  $<111>$  crystallographic orientation directions 57' which are parallel throughout the crystal and orientated with the  $<111>$  center axis, with fluoride crystal 52' having minimal crystal dislocation defects with a minimal uniform concentration.

Preferably lens 50 is comprised of a calcium fluoride crystal 52. Preferably the calcium fluoride crystal 52 has a 157 nm internal transmission  $> 99\%/cm$ . Preferably the calcium fluoride crystal has a 193 nm internal transmission  $> 99\%/cm$ . FIG. 6 shows a calcium fluoride crystal with the calcium fluoride  $<111>$  crystallographic orientation direction 57. The  $<111>$  is perpendicular to the corresponding calcium fluoride (111) plane.

Preferably fluoride crystal optical lithography lens 50 has a first curved optical surface 62 and a second curved optical surface 64 for manipulating lithography light, preferably lithography light  $\lambda < 200$  nm. In a preferred alternative fluoride crystal optical lithography lens 50 has a curved optical surface 66 and a planar optical surface 68.

Preferably the variation in crystallographic orientation 58 is in the range from about 2 to 15 degrees, preferably from 3 to 12, and most preferably 5 to 10 degrees. As shown in FIG. 5a and 7a the variation in  $\langle 111 \rangle$  orientation tilts away from the optical center axis 54  $\langle 111 \rangle$  direction orientation 60 and towards lens perimeters 56.

- 5 Preferably the crystal disorientation  $\theta$  progresses from the center axis with  $\theta < \theta_2 < \theta_3 < \theta_4 < \theta_5 < \theta_6 < \theta_7 \dots < \theta_n$ .

Preferably fluoride crystal optical lithography lens 50 has nonparallel light ray paths 72 and fluoride crystal 52 has nonparallel  $\langle 111 \rangle$  crystal paths 74 in alignment with the lens light ray paths 72. The crystallographic orientation direction  $\langle 111 \rangle$  crystal paths 74 are aligned with the light ray paths 72 that lens 50 is designed to manipulate. Preferably lens 50 and crystal paths 74 are utilized to coverage or diverge an incident light beam comprised of light rays.

The invention further includes a fluoride crystal optical lens 76 comprised of a single fluoride crystal 78. The fluoride crystal 78 has a first optical lens surface 80 and a separated second optical lens surface 82 which opposes the first. Fluoride crystal 78 has a progressive concentration 84 of crystal dislocation defects 86 that increase from the second optical lens surface 80. As shown in FIG. 7-8, the concentration of crystal dislocation defects is a progressive concentration represented by the arrow 84 with the concentration of defects 86 preferably increasing from the second surface 82 to the first 80. In a preferred embodiment the first optical lens surface is a curved lens surface and the second optical lens surface is a curved lens surface. In an alternative embodiment the first optical lens surface is a flat optical surface. In an alternative embodiment the second optical lens surface is a flat optical surface. Preferably lens 76 has an optical center axis 54 aligned with the local  $\langle 111 \rangle$  direction. In a preferred embodiment the single fluoride crystal 78 is calcium fluoride, preferably with a 193 nm internal transmission  $> 99\%/cm$  and a 157 nm internal transmission  $> 99\%/cm$ .

The invention further includes a calcium fluoride crystal optical element for manipulating a transmitting wavelength  $\lambda < 200$  nm. The less than 200 nm wavelength optical element 76 is comprised of a calcium fluoride crystal 78. The calcium fluoride crystal has a first optical surface 80 and a second optical surface 82 for manipulating  $\lambda$ . The calcium fluoride crystal has a concentration 84 of crystal dislocation defects 86 that increases from the second optical surface to the first optical surface. The first



optical surface has a first surface subgrain boundary length per unit area in the range from about 10 to 50 cm/cm<sup>2</sup>. The second optical surface has a second surface subgrain boundary length per unit area less than 10 cm/cm<sup>2</sup>. The element 76 has a large dimension D. Preferably D is greater than 100 mm, more preferably  $\geq 150$  mm, more preferably  $\geq 200$  mm, more preferably  $\geq 250$  mm, and most preferably  $\geq 300$ . In a preferred embodiment the first optical surface is a curved lens surface. In a preferred embodiment the second optical surface is a curved lens surface. In an alternative embodiment an optical surface is a flat optical surface. In a preferred embodiment  $\lambda$  is centered about 193 nm and the calcium fluoride crystal has a 193 nm internal transmission  $> 99\%/cm$ . In a further embodiment  $\lambda$  is centered about 157 nm and the calcium fluoride crystal has a 157 nm internal transmission  $> 99\%/cm$ . Preferably optical element 76 has a calcium fluoride crystal variation 58 in  $\langle 111 \rangle$  crystallographic orientation that tilts away and spreads out from a  $\langle 111 \rangle$  optical axis. Preferably the variation is at least three degrees, and more preferably at least five degrees.

15 The invention further includes a fluoride crystal lens blank. Fluoride crystal lens blank 100 is comprised of fluoride crystal 102. Fluoride crystal 102 has a center axis 104 through a large dimension D surface 106. Center axis 104 and surface 106 are encompassed by blank perimeter 108. Center axis 104 is aligned with and coincides with an optically preferred crystallographic direction 110. Fluoride crystal blank 100  
20 has a variation 158 in crystallographic orientation direction 112 which spreads out from and tilts away from center axis 104 and toward blank perimeter 108. Preferably fluoride crystal 102 is calcium fluoride. With calcium fluoride lens blank 100 the optically preferred crystal direction 110 is the calcium fluoride direction  $\langle 111 \rangle$ . Preferably calcium fluoride crystal 102 has a 193 nm internal transmission  $> 99\%/cm$ .  
25 Preferably the large dimension D of fluoride crystal lens blank 100 is  $\geq 100mm$ , more preferably  $D \geq 150$  mm, more preferably  $\geq 200$  mm, more preferably  $\geq 250$  mm, and most preferably  $D \geq 300$  mm. Preferably the variation 158 is crystallographic orientations 112 is in the range from about 2 to 15 degrees, more preferably 3 to 12 degrees, and most preferably 5 to 10 degrees. With a calcium fluoride crystal lens  
30 blank the variation 158 from the  $\langle 111 \rangle$  center axis 104 is at least 3 degrees, and more preferably  $\geq 5^\circ$ . As shown in FIG. 9a, blank 100 for forming into an optical element lens 76, 50 (such as shown by dashed lines inside blank 100), preferably has a second

surface 114 which opposes surface 106 with fluoride crystal 102 having a concentration of crystal dislocation defects 86 that increases from second surface 114 to surface 106. Preferably optical lens blank 100 as shown in FIG. 10 has a second surface 114 having a second surface subgrain boundary length per unit area SS and surface 106 having a large dimension surface subgrain boundary length per unit area FS wherein  $FS > SS$ . Preferably the second surface subgrain boundary length per unit area  $SS < 10 \text{ cm/cm}^2$ , and more preferably FS is in the range from about 10 to 50  $\text{cm/cm}^2$ . FIG. 11-12 show the subgrain boundaries of a calcium fluoride optical lens blank surface that has been acid etched. These photomicrographs are of the calcium fluoride surface after acid etching for 15 minutes with 0.1 N Nitric acid. FIG. 12 was analyzed with quantitative optical microscopy to measure subgrain boundary characteristics including subgrain boundary length per unit area. FIG. 12 calcium fluoride optical blank surface has a subgrain boundary length per unit area of  $15 \text{ cm/cm}^2$  and the average size of subgrains is about 1.8 mm in diameter.

The invention further includes a birefringence minimizing fluoride crystal optical lithography lens blank. The optical element blank comprises a calcium fluoride crystal having a 193 nm internal transmission  $>99\%/ \text{cm}$  and a refractive index homogeneity no greater than 1 ppm. As shown in FIG. 13, calcium fluoride blank 100 has a plurality of non-parallel crystallographic  $\langle 111 \rangle$  orientations. Blank 100 has an optical center axis 104 which coincides with the local calcium fluoride crystal  $\langle 111 \rangle$  direction. The blank has a variation in crystallographic orientation direction wherein the angular deviation  $\theta$  between the center axis 104 and a non-parallel crystallographic  $\langle 111 \rangle$  orientation at a given location having a relative location distance between the center axis 104 and the perimeter 108 correlates to the relative distance between the given location and axis 104. As shown in FIG. 13, 9 and 9a blank 100 preferably has a first surface 106 and a second surface 114 with crystal dislocation defects 86 that increase from the second surface 114 to the first surface 106. Preferably the first and second surfaces are normal to the center axis, with blank 100 preferably in the shape form of a cylindrical disk of the appropriate size for the blank to be the preform of the optical element it is to be formed and shaped into. Preferably blank 100 has a first surface 106 and a second surface 114 with the second surface 114 having a second surface subgrain boundary length per unit area (designated by SS)  $< 10 \text{ cm/cm}^2$

and the first surface 106 having a first surface subgrain boundary length per unit area (designated by FS)  $\geq 10 \text{ cm/cm}^2$ . Preferably the first surface subgrain boundary length per unit area is in the range from about 10 to 50  $\text{cm/cm}^2$ .

The invention further includes a fluoride crystal optical element blank. The  
5 blank is preferably comprised of a single fluoride crystal, most preferably a calcium fluoride crystal. Optical element blank 100 has a diameter D, a first diameter plane surface 106, a second diameter plane surface 114, and a crystal thickness TH between the first and second surfaces. Blank 100 has a concentration 84 of crystal dislocation defects 86 that increases from the second surface 114 to the first surface 106, and the  
10 second surface 114 has a second surface subgrain boundary length per unit area SS and the first surface 106 has a first surface subgrain boundary length per unit area FS wherein  $FS > SS$ . Preferably SS is less than 10  $\text{cm/cm}^2$ . Preferably FS is in the range from about 10 to 50  $\text{cm/cm}^2$ .

It will be apparent to those skilled in the art that various modifications and  
15 variations can be made to the present invention without departing from the spirit and scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

## Claims:

1. A birefringence minimizing fluoride crystal VUV optical lithography lens, said lens comprising a fluoride crystal, said fluoride crystal lens having an optical center  
5 axis encompassed by a fluoride crystal lens perimeter, said fluoride crystal lens having a variation in crystallographic orientation direction which tilts away from the optical center axis towards said fluoride crystal lens perimeter.
2. A lens as claimed in claim 1, wherein said fluoride crystal is a calcium fluoride  
10 crystal.
3. A lens as claimed in claim 1, wherein said fluoride crystal optical lithography lens has a first curved optical surface and a second curved optical surface.
- 15 4. A lens as claimed in claim 1, wherein said fluoride crystal optical lithography lens has a curved optical surface and a planar optical surface.
5. A lens as claimed in claim 1, wherein the variation in crystallographic orientation is in the range from about 2 to 15 degrees.  
20
6. A lens as claimed in claim 1, wherein the variation in crystallographic orientation is in the range from about 3 to 12 degrees.
7. A lens as claimed in claim 1, wherein the variation in crystallographic  
25 orientation is in the range from about 5 to 10 degrees.
8. A lens as claimed in claim 1, wherein said lens has a plurality of light ray paths and said fluoride crystal includes a plurality of  $\langle 111 \rangle$  crystal paths in alignment with said lens light ray paths.  
30
9. A fluoride crystal optical lens, said fluoride crystal optical lens comprised of a single fluoride crystal having a first optical lens surface and a separated second optical

lens surface, said second optical lens surface opposing said first optical lens surface, said fluoride crystal having a progressive concentration of crystal dislocation defects that increases from said second optical lens surface to said first optical lens surface.

5 10. A lens as claimed in claim 9, wherein said first optical lens surface is a curved lens surface and said second optical lens surface is a curved lens surface.

11. A lens as claimed in claim 9, wherein said first optical lens surface is a flat optical surface.

10

12. A lens as claimed in claim 9, wherein said second optical lens surface is a flat optical surface.

13. A lens as claimed in claim 9, wherein said lens has an optical center axis  
15 aligned with a local  $\langle 111 \rangle$  direction.

14. A lens as claimed in claim 9, wherein said fluoride crystal is calcium fluoride.

15. A lens as claimed in 13, wherein said calcium fluoride crystal has a 193 nm  
20 internal transmission  $>99\%/cm$ .

16. A calcium fluoride crystal optical element for manipulating a transmitting wavelength  $\lambda < 200$  nm, said element comprising a calcium fluoride crystal having a first optical surface and a second optical surface for manipulating  $\lambda$ , said calcium  
25 fluoride crystal having a concentration of crystal dislocation defects that increases from said second optical surface to said first optical surface, said first optical surface having a first surface subgrain boundary length per unit area in the range from about 10 to 50  $cm/cm^2$ , said second optical surface having a second surface subgrain boundary length per unit area  $< 10$   $cm/cm^2$ .

30

17. An optical element as claimed in claim 16, said element having a large dimension D, wherein  $D \geq 100$  mm.

18. An optical element as claimed in claim 16, said element having a large dimension  $D$ , wherein  $D \geq 150$  mm.
- 5 19. An optical element as claimed in claim 16, said element having a large dimension  $D$ , wherein  $D \geq 200$  mm.
20. An optical element as claimed in claim 16, said element having a large dimension  $D$ , wherein  $D \geq 250$  mm.
- 10 21. An optical element as claimed in claim 16, said element having a large dimension  $D$ , wherein  $D \geq 300$  mm.
- 15 22. An optical element as claimed in claim 16, wherein said first optical surface is a curved lens surface.
23. An optical element as claimed in claim 16, wherein said second optical surface is a curved lens surface.
- 20 24. An optical element as claimed in claim 16, wherein said wavelength  $\lambda$  is centered about 193 nm and said calcium fluoride crystal has a 193 nm internal transmission  $> 99\%/cm$ .
- 25 25. An optical element as claimed in claim 16, wherein said wavelength  $\lambda$  is centered about 157 nm and said calcium fluoride crystal has a 157 nm internal transmission  $> 99\%/cm$ .
- 30 26. An optical element as claimed in claim 17, said calcium fluoride crystal having a variation in  $\langle 111 \rangle$  crystallographic orientation that tilts away and spreads out from a  $\langle 111 \rangle$  optical axis.

27. An optical element as claimed in claim 26, wherein said variation is at least three degrees.
28. An optical element as claimed in claim 26, wherein said variation is at least five  
5 degrees.
29. A fluoride crystal lens blank, said lens blank comprising a fluoride crystal having an axis through a large dimension D surface, said axis and said large dimensions D surface encompassed by a blank perimeter, said axis aligned and coinciding with an  
10 optically preferred crystallographic direction of said fluoride crystal, said fluoride crystal lens blank having a variation in crystallographic orientation direction which spreads out from said axis and tilts away from said axis and towards said blank perimeter.
- 15 30. A lens blank as claimed in claim 29, wherein said fluoride crystal is calcium fluoride.
31. A lens blank as claimed in claim 29, wherein said large dimension  $D \geq 100$  mm.
- 20 32. A lens blank as claimed in claim 29, wherein the variation in crystallographic orientation is in the range from about 2 to 15 degrees.
33. A lens blank as claimed in claim 29, said blank having a second surface, said second surface opposing said large dimension surface, said fluoride crystal having a  
25 concentration of crystal dislocation defects that increases from said second surface to said large dimension surface.
34. A lens blank as claimed in claim 29, said blank having a second surface, said second surface opposing said large dimension surface, said second surface having a  
30 second surface subgrain boundary length per unit area SS and said large dimension surface having a large dimension surface subgrain boundary length per unit area FS wherein  $FS > SS$ .

35. A lens blank as claimed in claim 34 wherein  $SS < 10 \text{ cm/cm}^2$ .
36. A lens blank as claimed in claim 34 wherein FS is in the range from about 10 to  
5  $50 \text{ cm/cm}^2$ .
37. A birefringence minimizing fluoride crystal optical lithography lens blank, said blank comprising a calcium fluoride crystal having a 193 nm internal transmission  $> 99\%/cm$  and a refractive index homogeneity  $\leq 1 \text{ ppm}$ , and a plurality of non-parallel  
10 crystallographic  $\langle 111 \rangle$  orientations, said blank having an optical center axis coinciding with a local calcium fluoride crystal  $\langle 111 \rangle$  direction, said blank having a crystal perimeter and a variation in crystallographic orientation direction wherein an angular deviation between the center axis and a non-parallel crystallographic  $\langle 111 \rangle$  orientation at a given location between said center axis and said perimeter correlates to a distance  
15 between said given location and said center axis.
38. A blank as claimed in claim 37, wherein said blank has a first surface and a second surface, said crystal having a concentration of crystal dislocation defects that increases from the second surface to the first surface.  
20
39. A blank as claimed in claim 37, wherein said blank has a first surface and a second surface, said second surface having a second surface subgrain boundary length per unit area  $< 10 \text{ cm/cm}^2$  and said first surface having a first surface subgrain boundary length per unit area  $\geq 10 \text{ cm/cm}^2$ .  
25
40. A blank as claimed in claim 37, wherein said blank has a first surface and a second surface, said first and second surfaces normal to said center axis, said second surface having a second surface subgrain boundary length per unit area  $< 10 \text{ cm/cm}^2$  and said first surface having a first surface subgrain boundary length per unit area in the  
30 range from about 10 to  $50 \text{ cm/cm}^2$ .



41. A fluoride crystal optical element blank, said blank comprised of a fluoride crystal having a diameter, a first diameter plane surface, a second diameter plane surface, and a crystal thickness defined by said first and second surfaces, said blank having a concentration of crystal dislocation defects that increases from said second surface to said first surface and said second surface having a second surface subgrain boundary length per unit area SS and said first surface having a first surface subgrain boundary length per unit area FS wherein  $FS > SS$ .
42. A blank as claimed in claim 41 wherein,  $SS < 10 \text{ cm/cm}^2$ .
43. A blank as claimed in claim 41, wherein FS is in the range of about 10 to 50  $\text{cm/cm}^2$ .

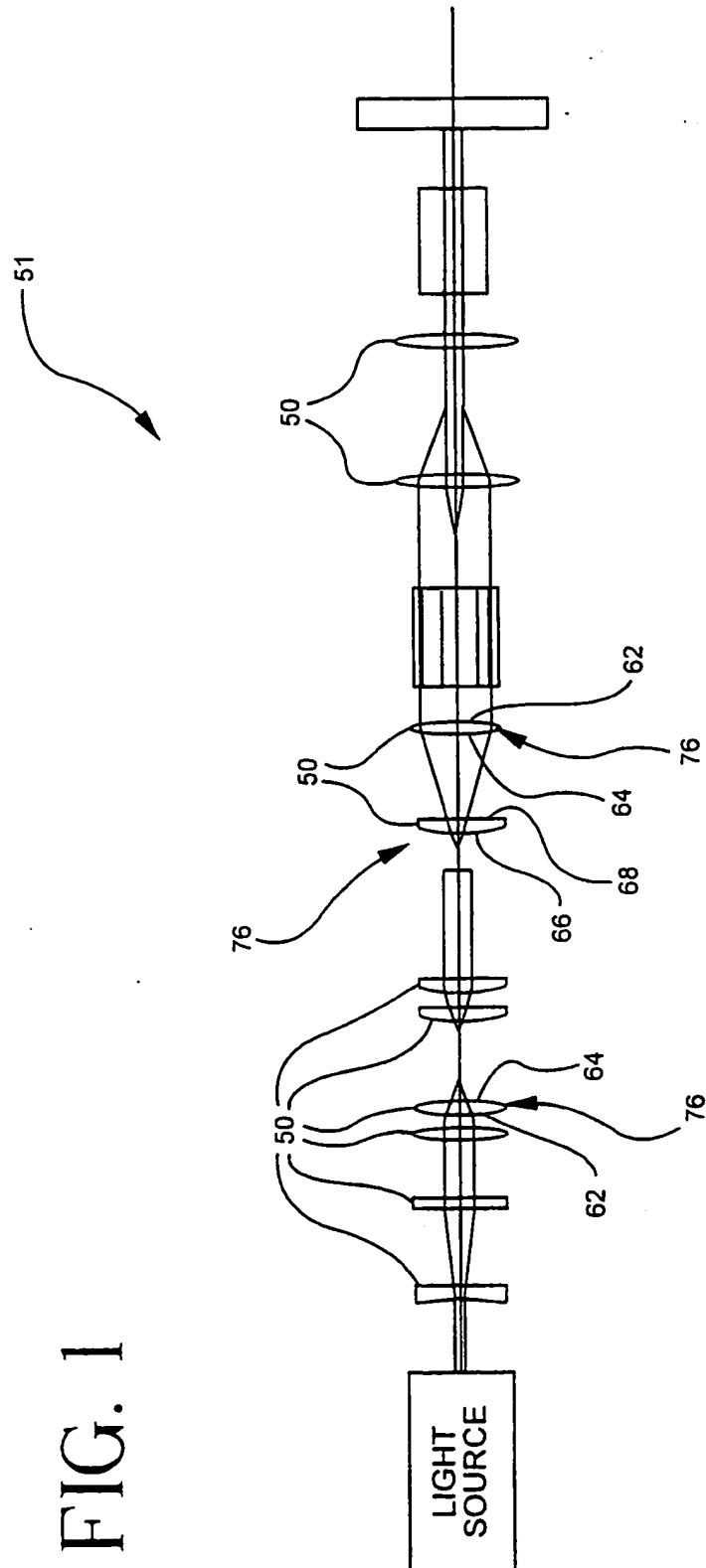


FIG. 2

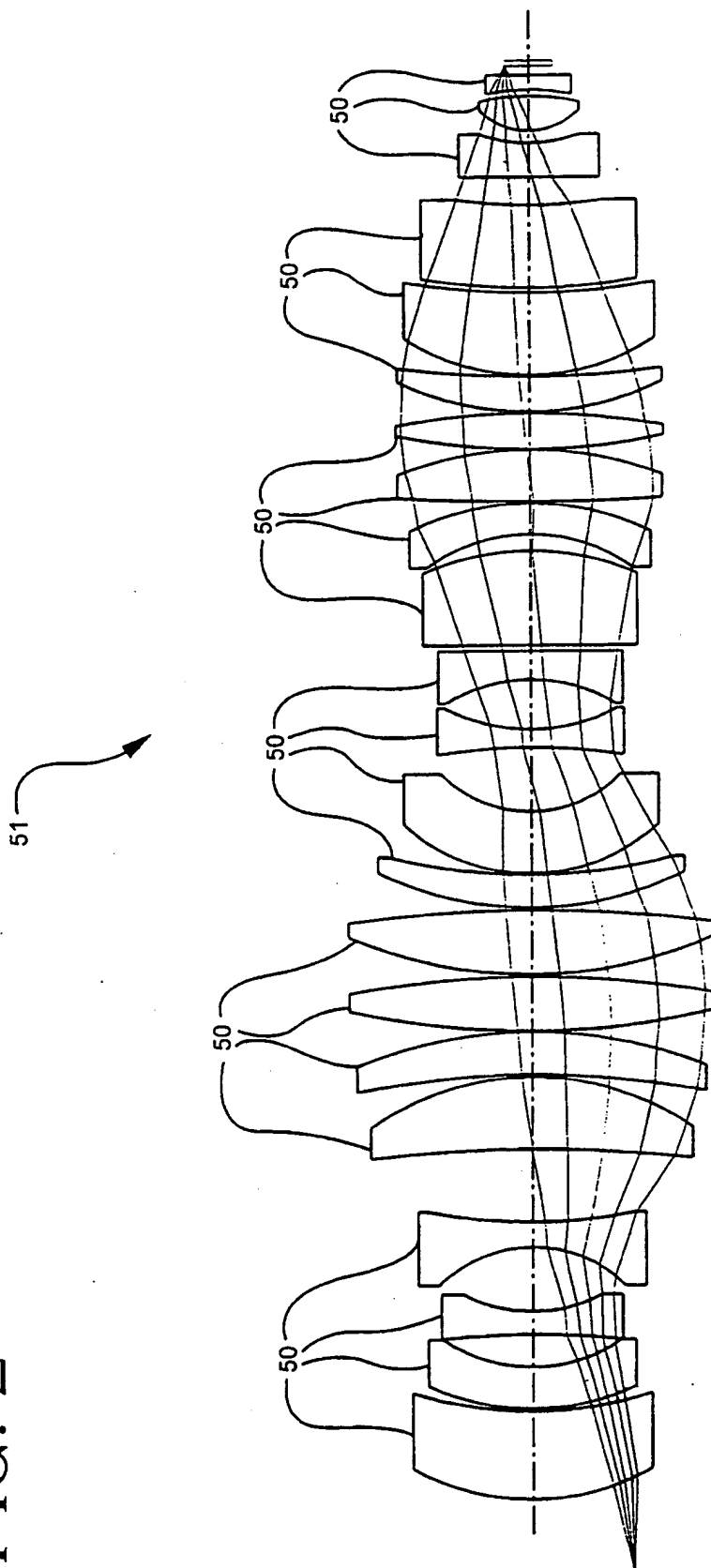


FIG. 2D

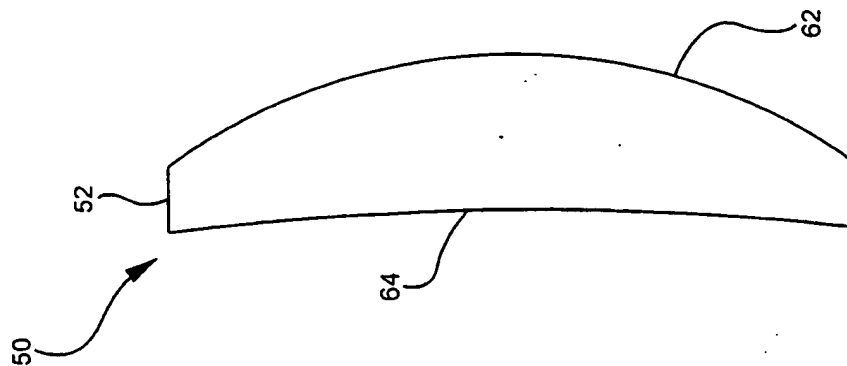


FIG. 2C

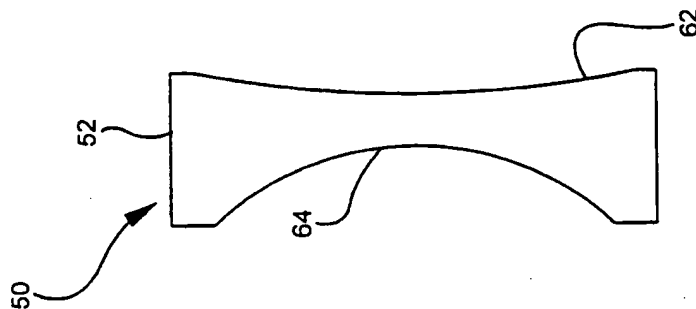


FIG. 2B

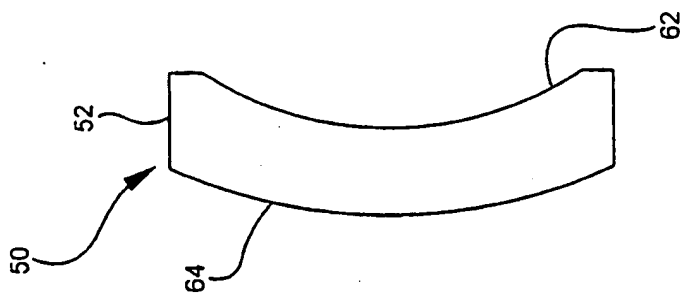


FIG. 2A

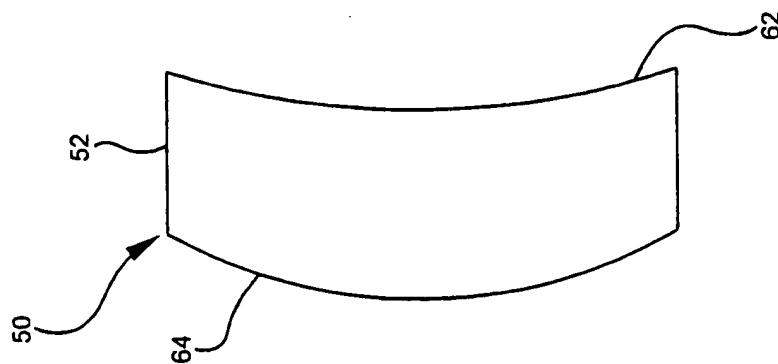


FIG. 2E

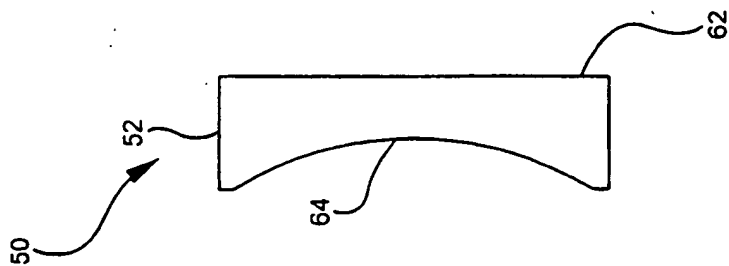


FIG. 2F

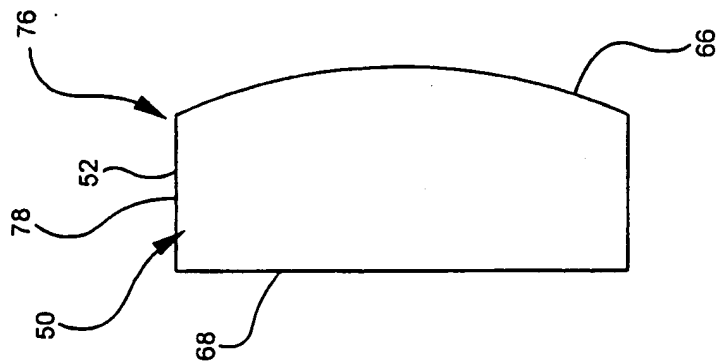


FIG. 2G

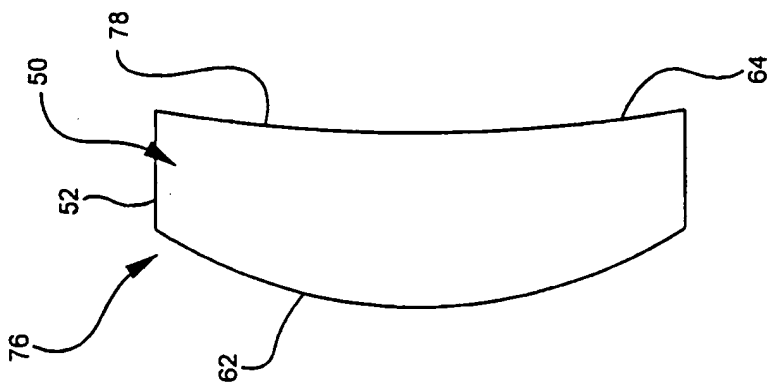
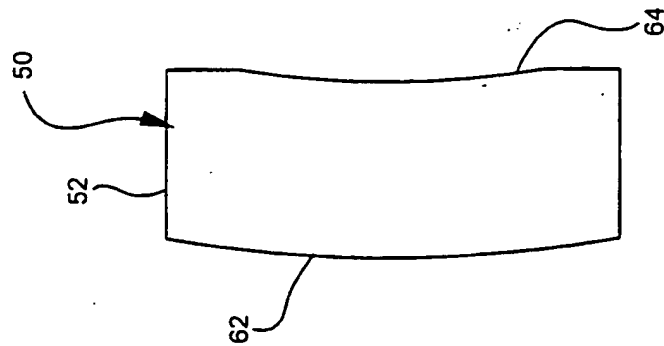


FIG. 2H



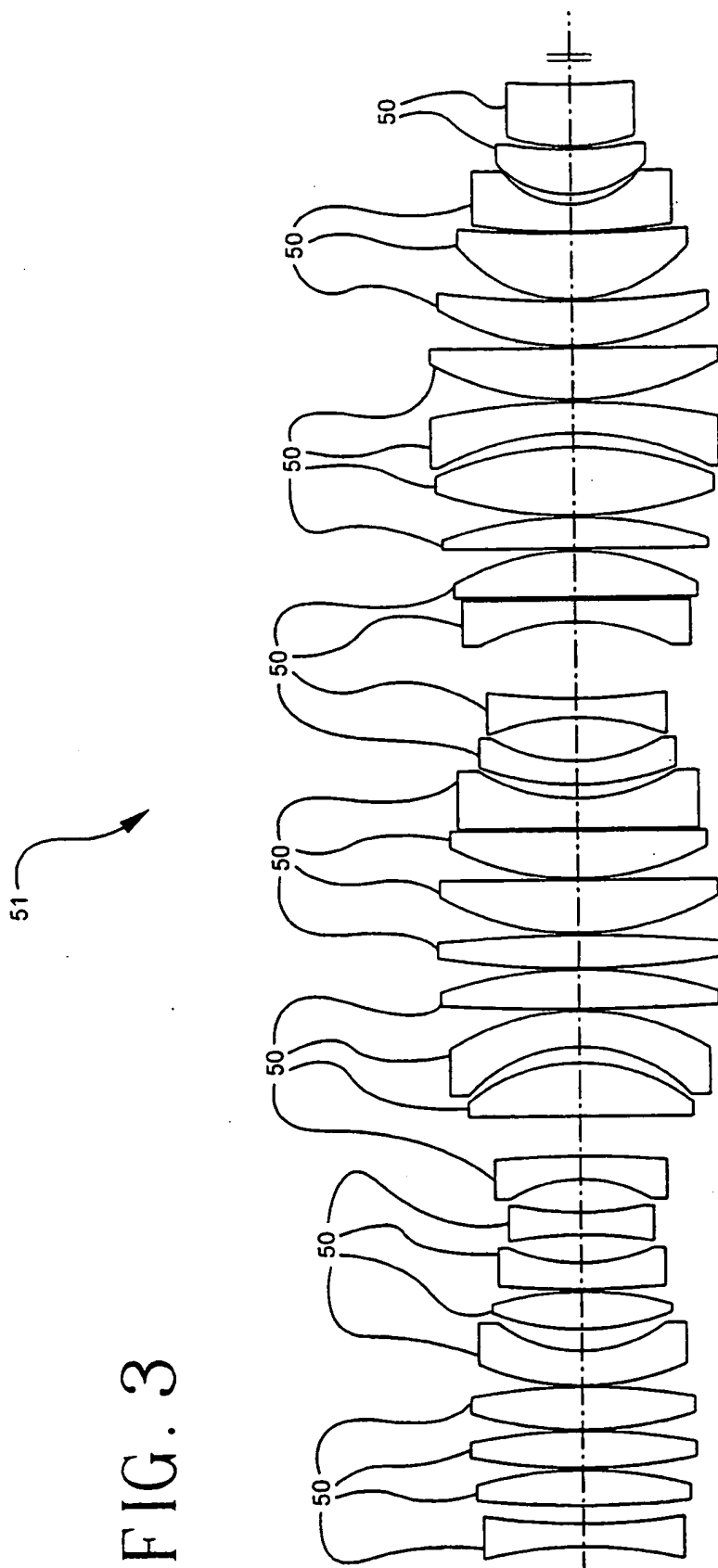


FIG. 3

FIG. 3D

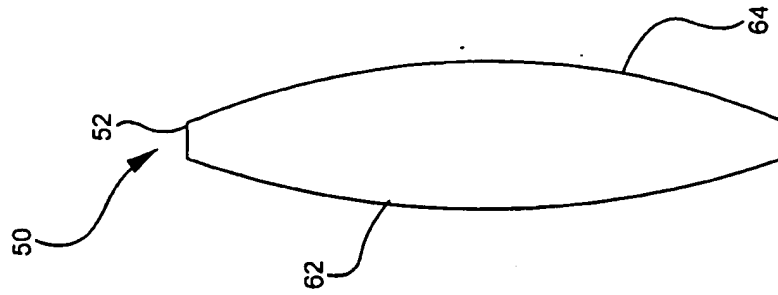


FIG. 3C

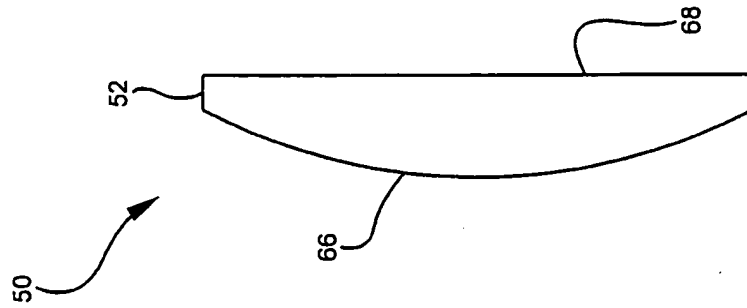


FIG. 3B

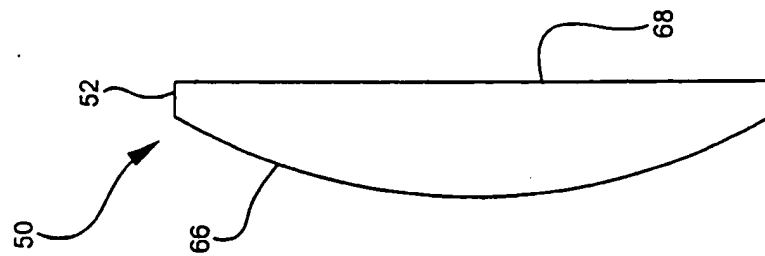


FIG. 3A

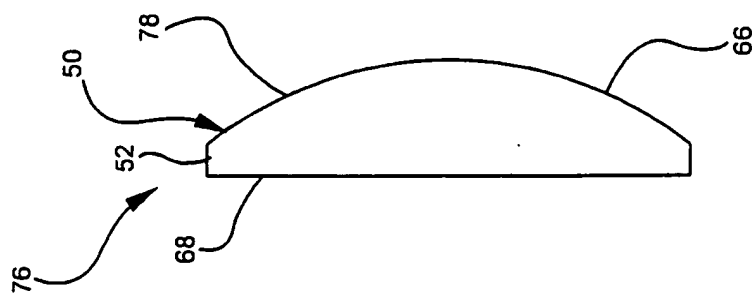


FIG. 3G

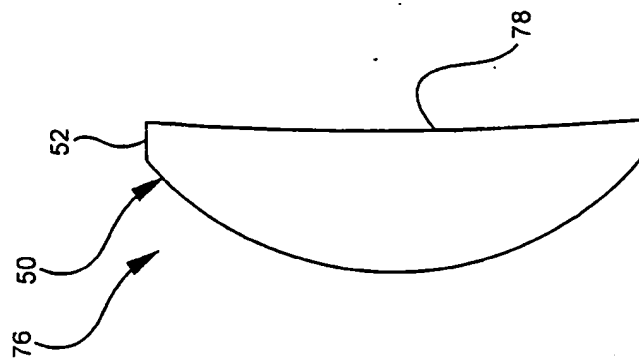


FIG. 3F

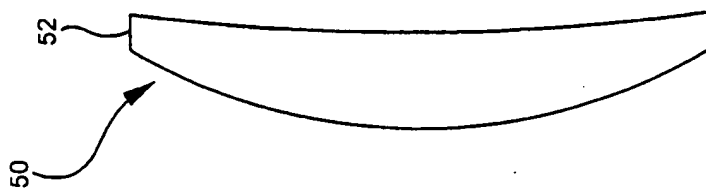
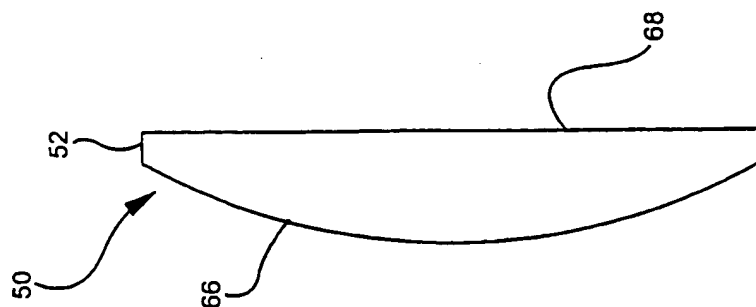


FIG. 3E





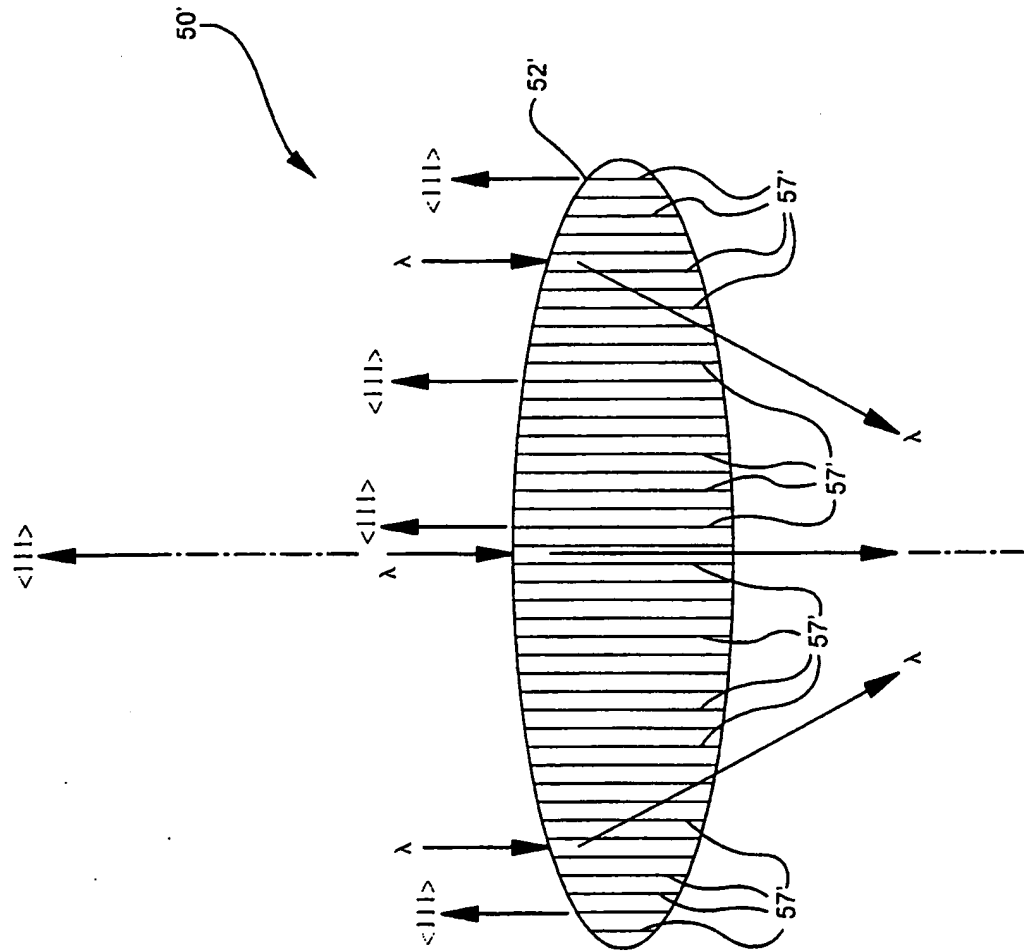


FIG. 4

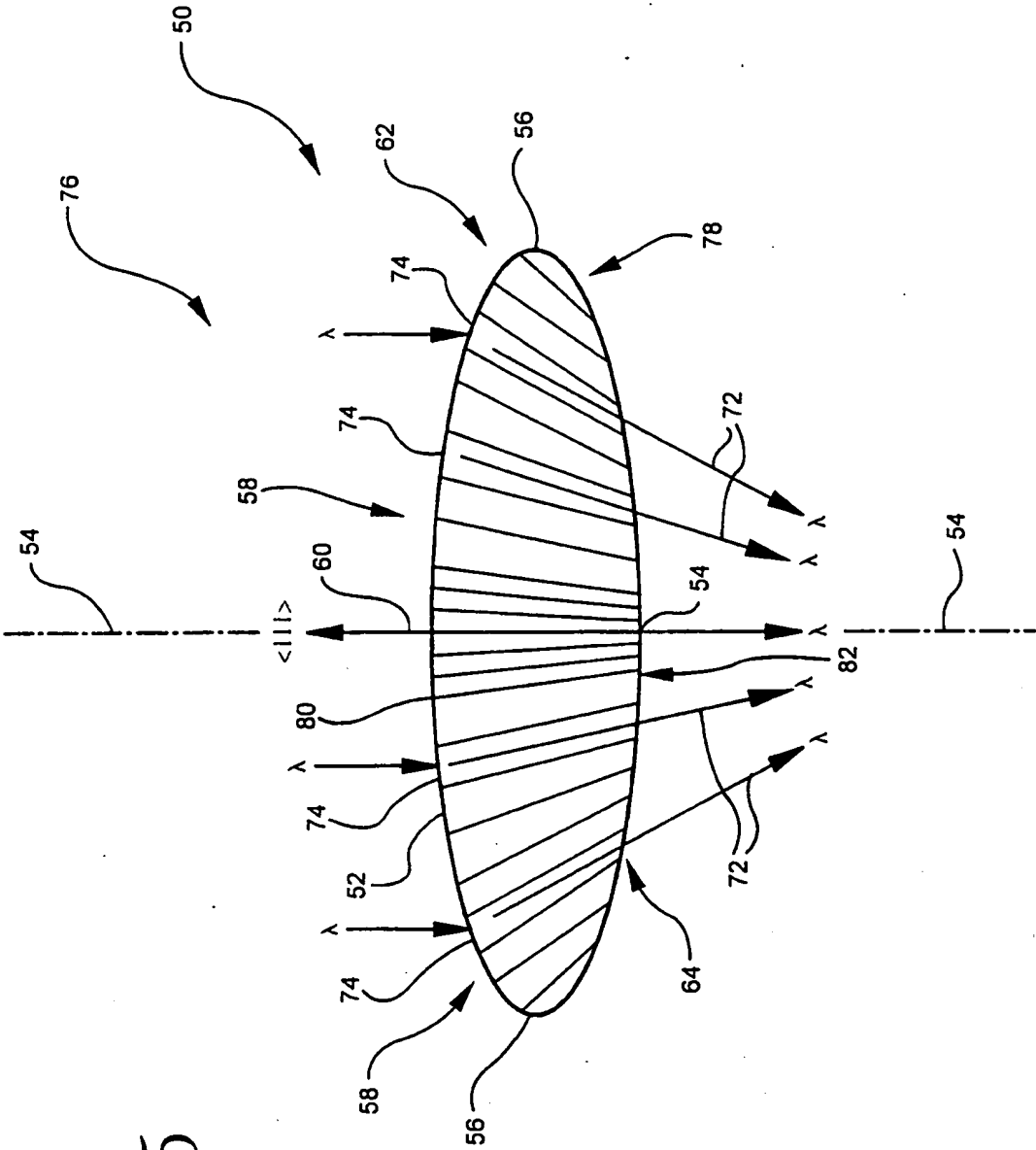


FIG. 5

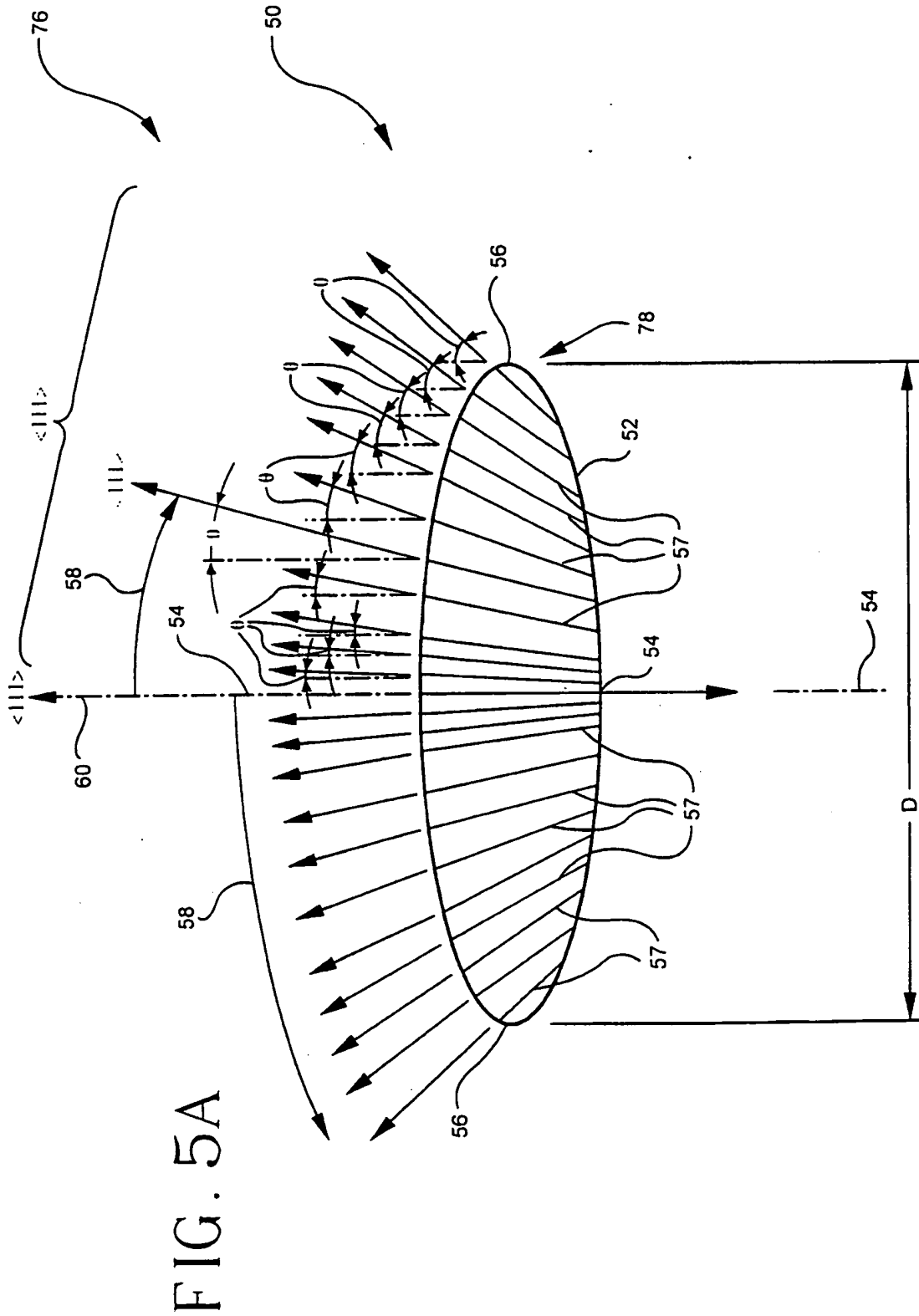


FIG. 6

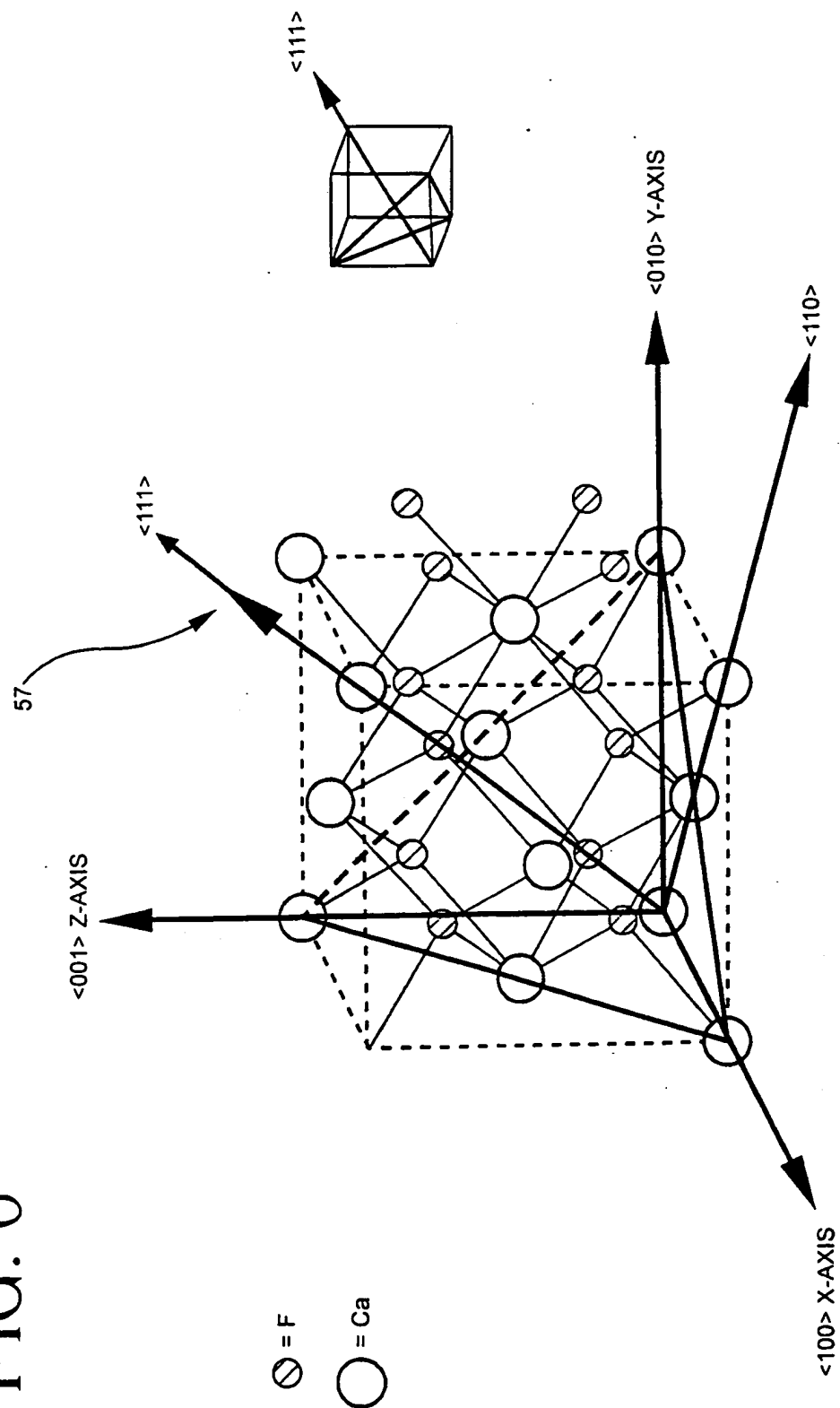
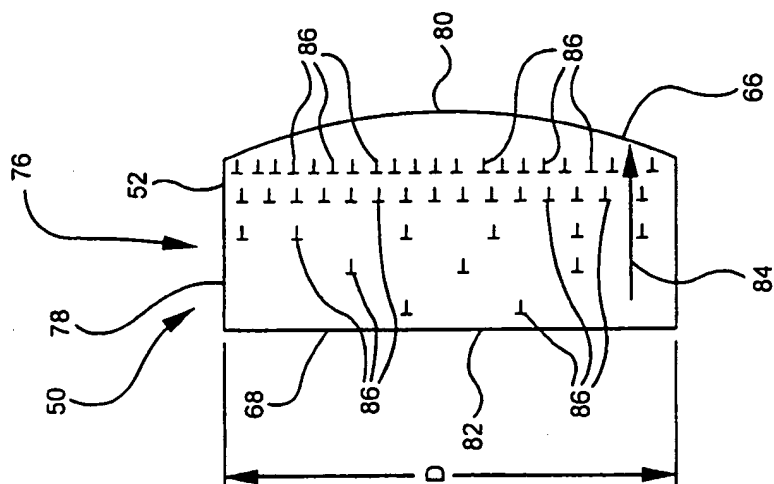


FIG. 7



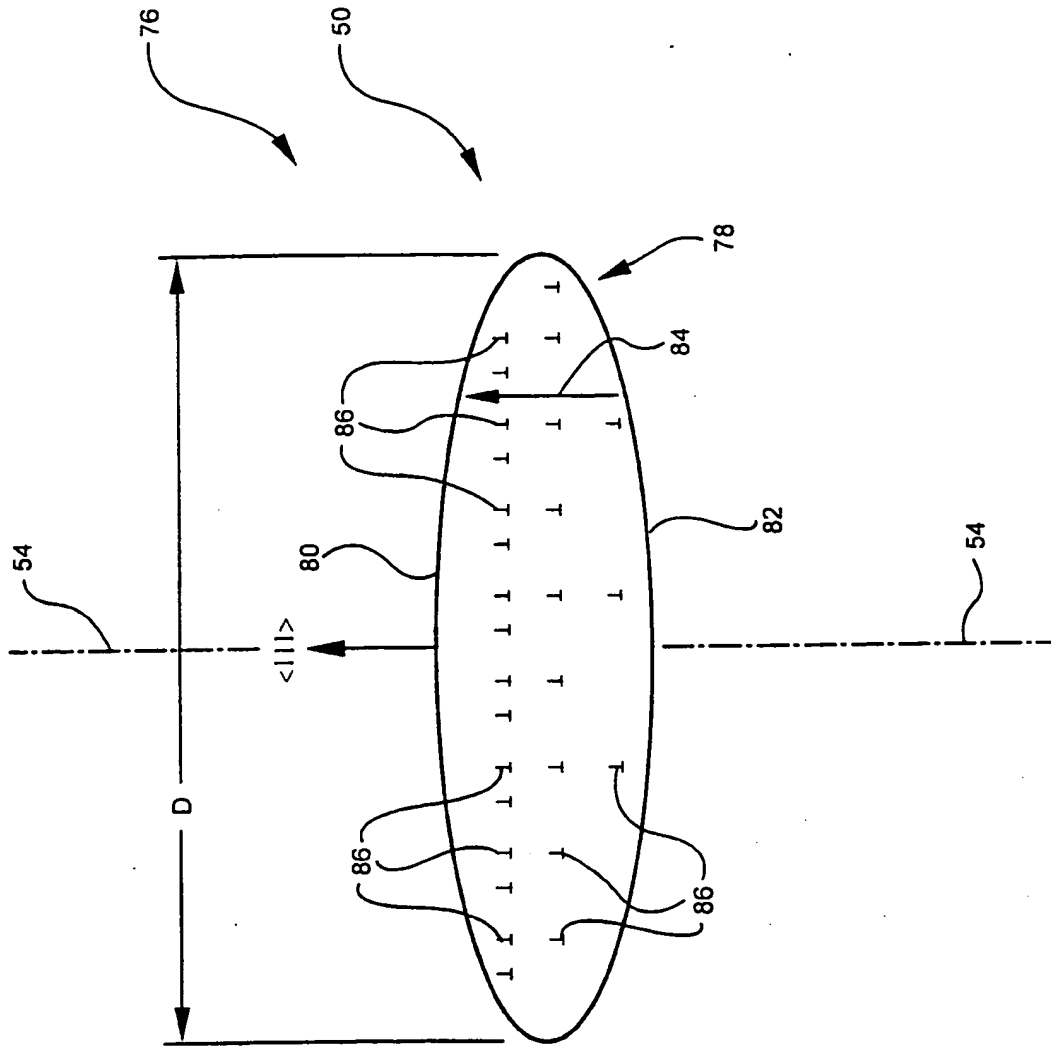


FIG. 8

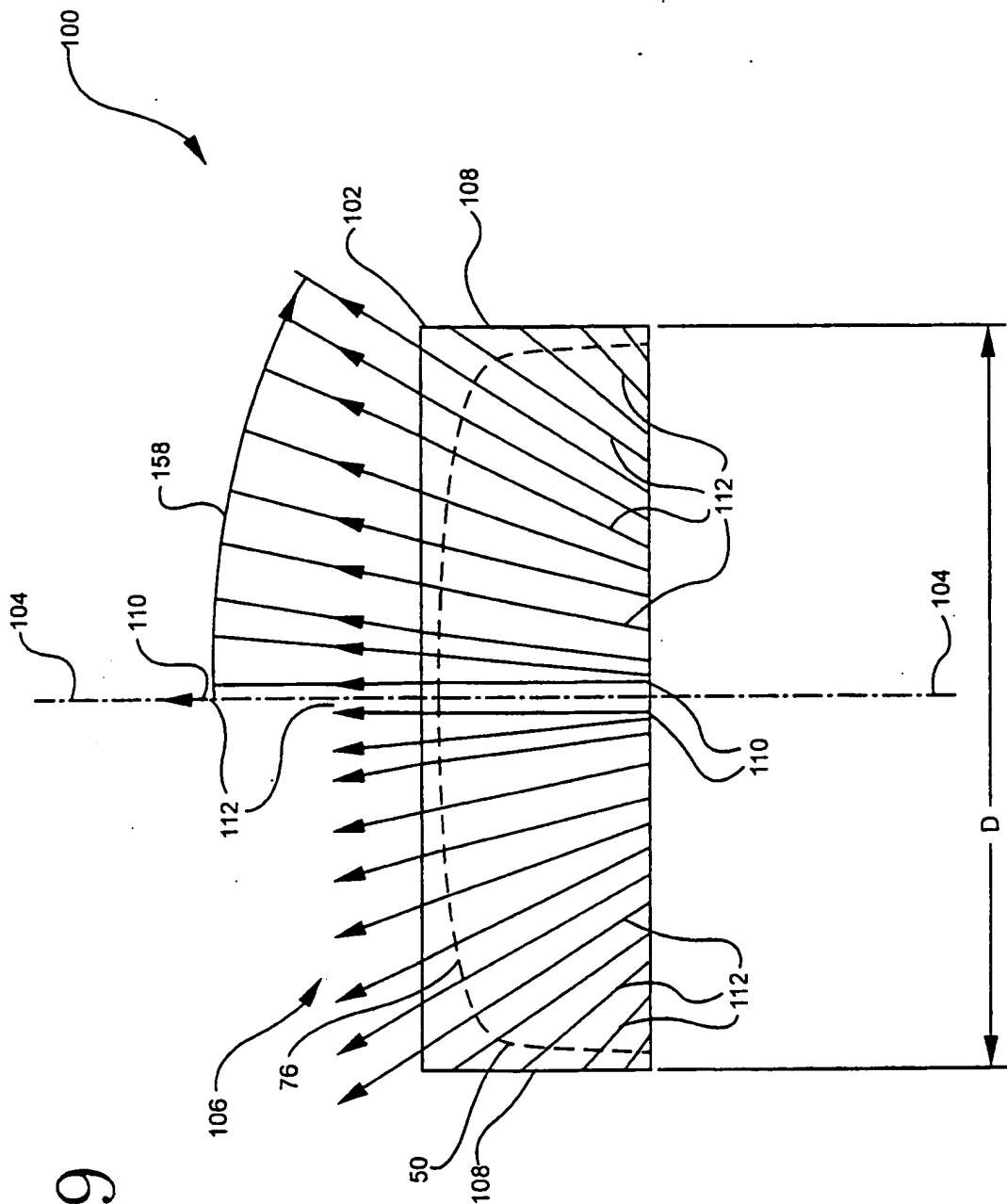


FIG. 9

FIG. 9A

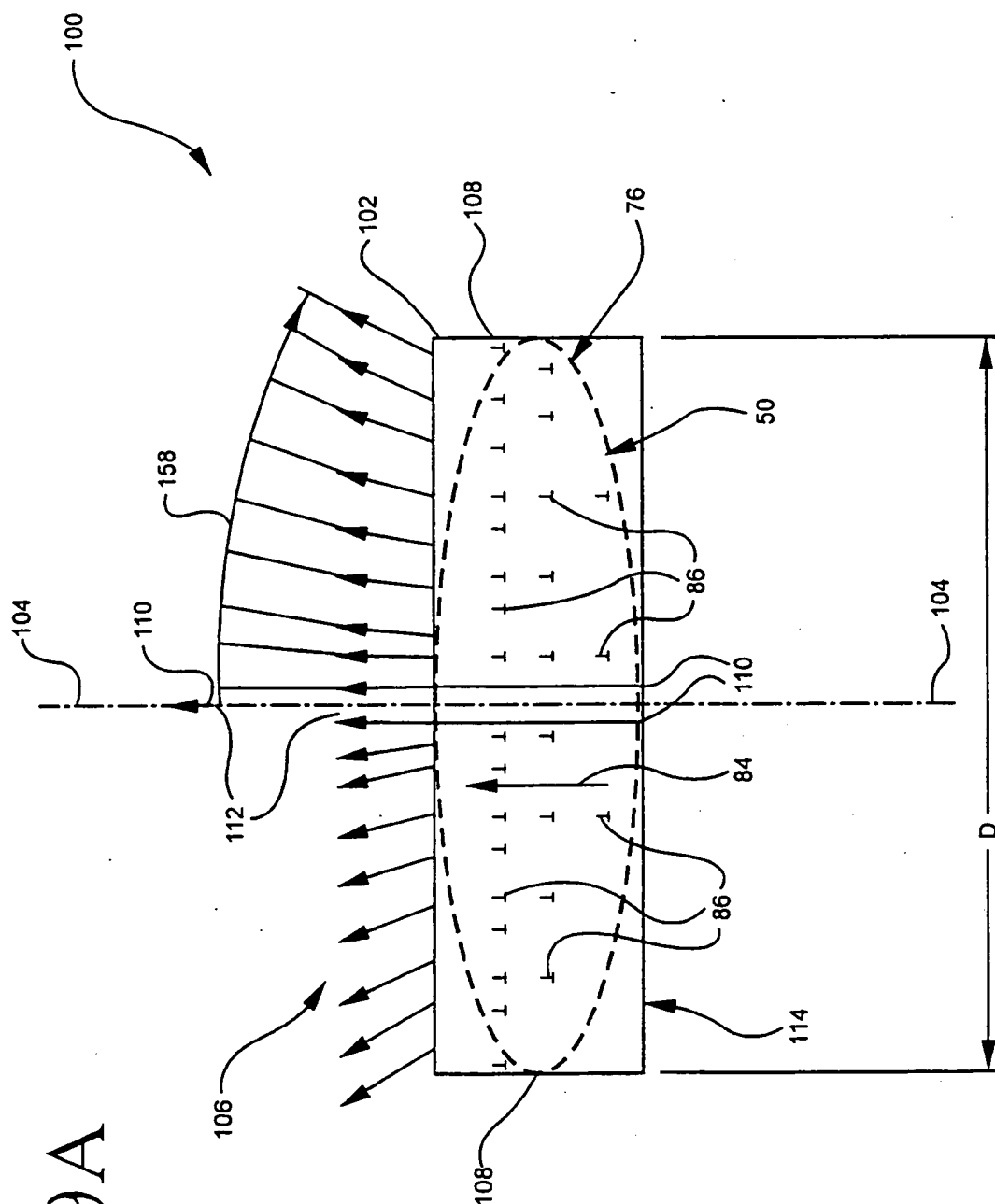




FIG. 10

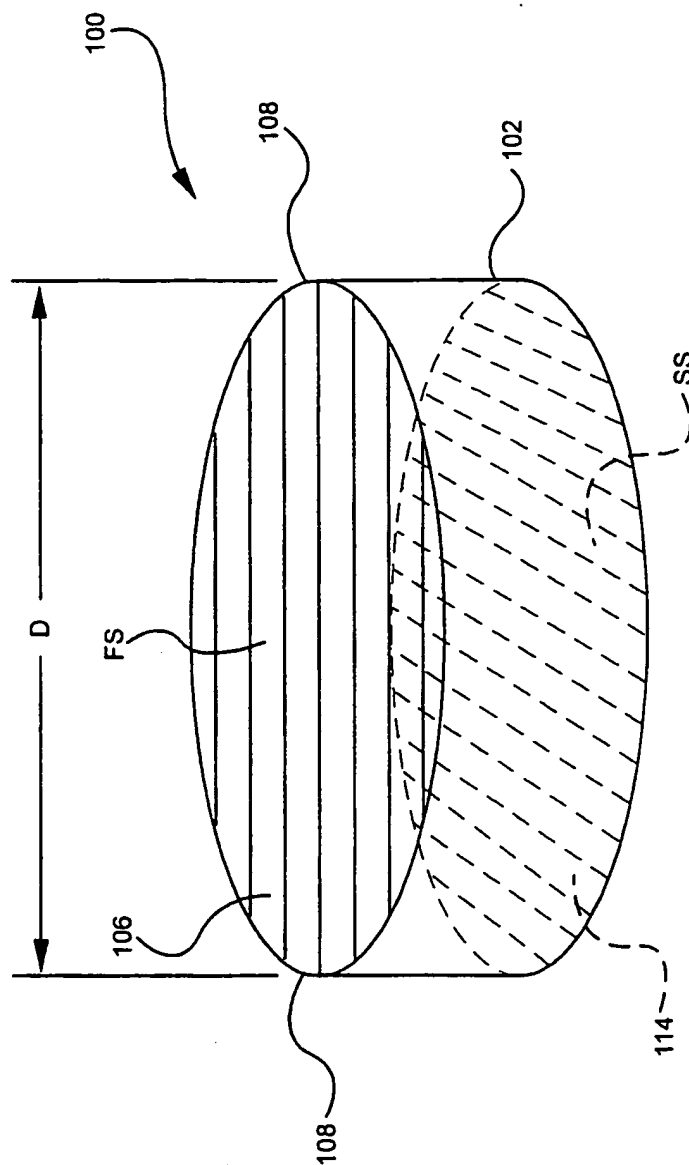


FIG. 11

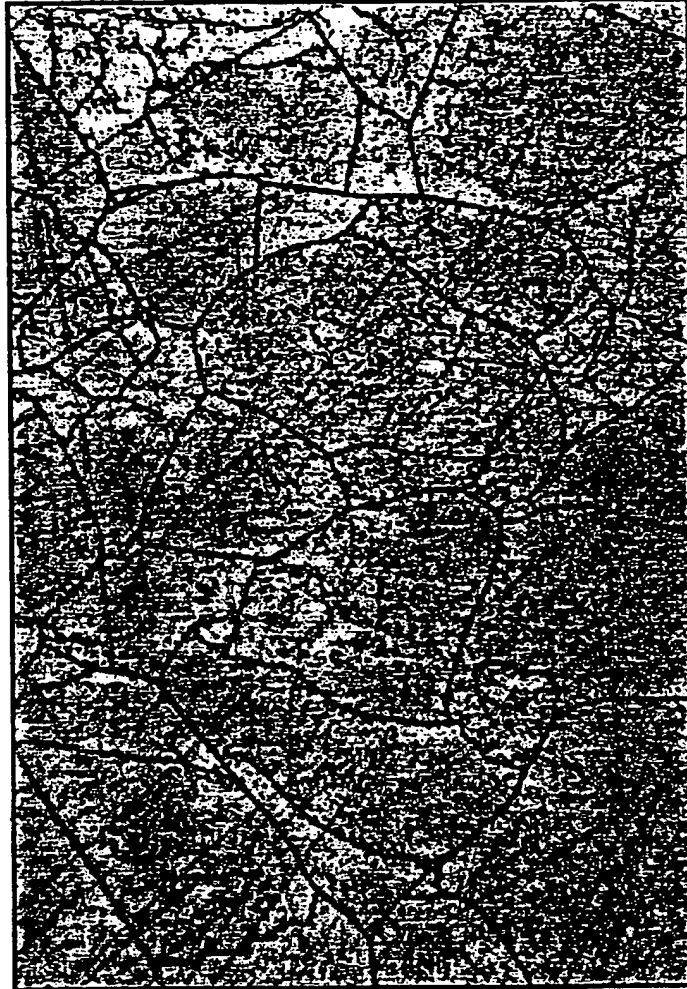


FIG. 12

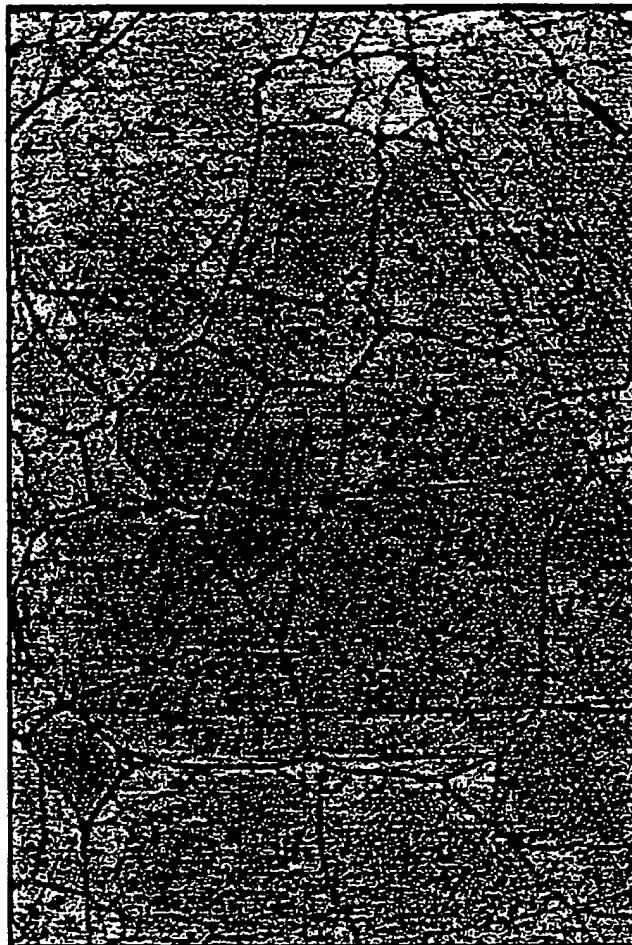


FIG. 12

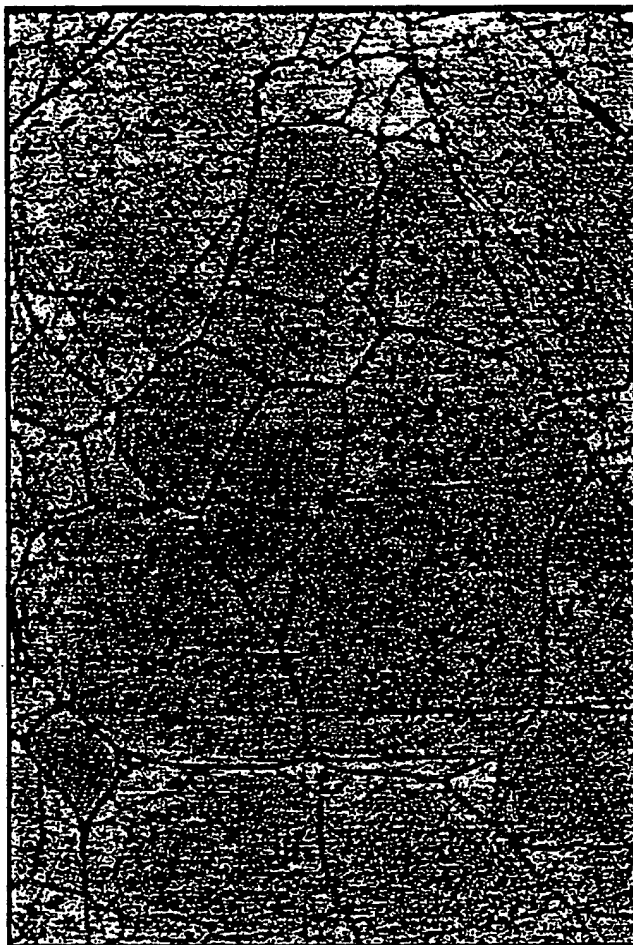


FIG. 13

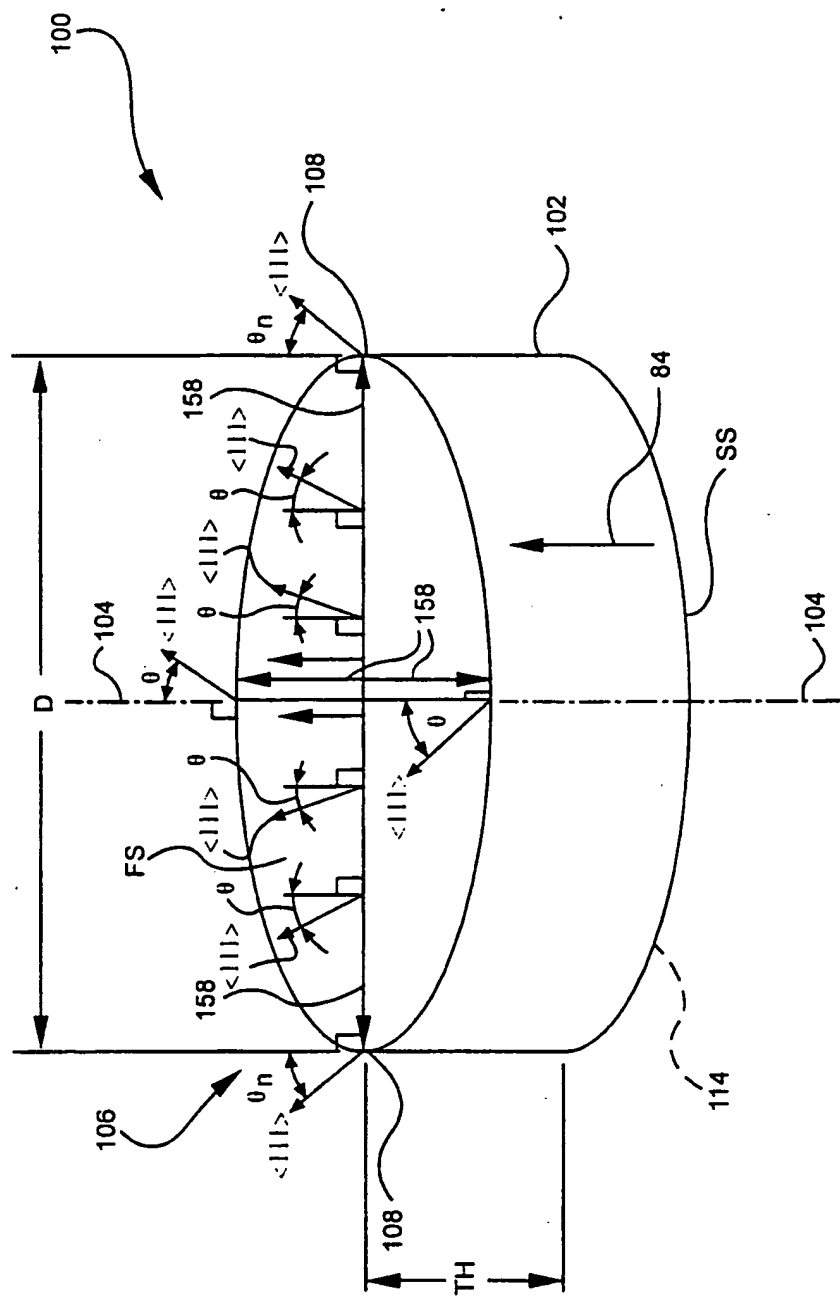
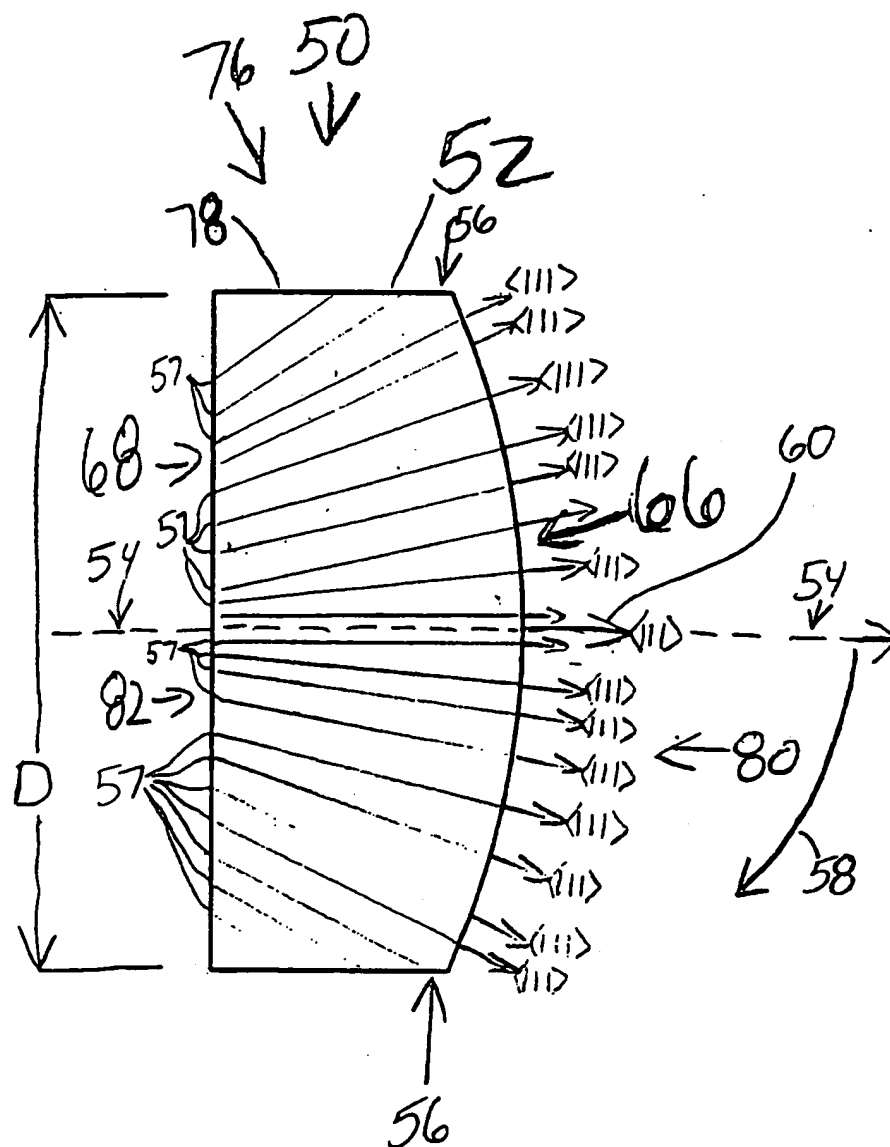


FIG. 7a



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/17165

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : G02B 13/14, 9/00; F21V 9/06

US CL : 359/350, 355, 361, 796

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 359/350, 355, 361, 796

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
EAST

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,031,977 (GIBSON) 16 Ju/y 1991 (16.07.1991), see entire document and particularly figure 3.	1-43
A,P	US 6,061,174 (SHIOZAWA et al.), 09 May 2000 (09.05.2000), see abstract as well as entire document	1-43

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

06 SEPTEMBER 2000

Date of mailing of the international search report

04 OCT 2000

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JARED TREAS

Telephone No. (703) 308-3174

**THIS PAGE BLANK (USPTO)**